UTILIZATION OF FURAN. V

Procedure and Apparatus for the Conversion of Furfurol to Furan by means of a Heterogeneous Catalytic Process in the Vapour Phase

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(Received November 30, 1966)

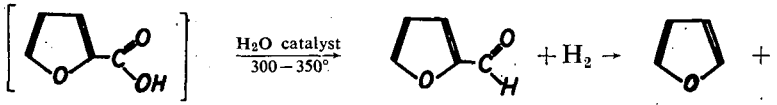
A catalytic laboratory has been developed for the oxidative decarboxylation of furfurol to furan. In contradistinction to the procedures known hitherto, the reaction was carried out in the vapour phase under oxidative conditions in the presence of the following catalysts: V_2O_5 on Al_2O_3, PbO on Al_2O_3, and PbO on aluminium grease supporter, respectively. The optimum parameters for the oxidative decarboxylation reaction have been determined.

Furan is one of the most important basic materials of modern organic chemical industry. Its utilization as basic material is made reasonable mainly by its accessibility from agricultural waste-materials and, on the other hand, by its numerous conversions to important industrial products.

All furan production procedures of industrial significance fall under either of the following two classes. Those methods belonging to the first one are characterized by catalytic decarbonylation of furfurol. The process max be illustrated by the following general equation (Equation 1):

(1)

In the processes of the second group fluoric acid intermediary product is formed, which, under the conditions applied, is unstable and decomposes to furan and carbon dioxide. In a number of cases the process takes place under reductive conditions, in hydrogen stream. These processes are characterized by the following general equation (Equation 2):



$$+CO_2+6{,}3\ \text{cal} \qquad (2)$$

1. *Catalytic decarbonylation of furfurol*

There are several methods known for the catalytic decarbonylation of furfurol. According to WILSON [1] the conversion may be accomplished in hydrogen atmosphere at 280—290° with nickel or cobalt catalyst. Generally, the oxides of the VIIIth

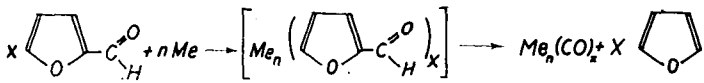
column of the periodic system proved suitable catalysts [2] under atmospheric or decreased pressure, in oxygen-free medium or in slight hydrogen stream.

According to ESCHINAZI's procedure [3] furfurol is heated in the presence of platinum catalyst and thus furan is yielded again.

A great number of catalytic furan production procedures are carried out in the presence of water vapours (steam). Among such conditions, with the simultaneous application of metal alloy catalysts at 300—500° furfural affords furan and carbon dioxide and hydrogen by-products. There are several assumptions concerning the formation of furan under the conditions given. According to the most obvious explanation the oxygen of water would oxidize the formyl group to carboxylic group and, since the process proceeds above the temperature of decarboxylation, the furoic acid decomposes to furan and carbon dioxide. The process is called decarbonylation, though the endgas contains only traces of carbon monoxide, while carbon dioxide and hydrogen are present near in stoichiometric ratio. Even the carbon monoxide traces present might be formed through the reduction of carbon dioxide [4]. According to WITHMAN's patent furan may be obtained from furfurol in 85—90% yield [4]. The catalyst applied was ZnO modified with Cs-, W-, Mo-, or V-oxides. The furfurol vapours were mixed with steam in molar ratio of 2:1—6:1 and passed through the catalyst above 200 °C. KARMILCIKS and HILLERS [5] succeeded in obtaining as high as 95% yields of furan from furfurol by passing water-furfurol 25:1 mixture through a catalyst consisting of a mixture of Al-, Cr-, Zn-, and Mn-oxides at 450°. The dilute aqueous furfural solution obtained by hydrolysis of pentosans proved a suitable starting material even without isolation of furan. However, in this case the activity of the catalyst was decreased because of the hydrocarbons deposited on its surface.

The processes catalysed by metal chromites provide lower yields. Passing furfurol and steam through Mn chromite catalyst containing K_2CrO_4 at 400° afforded only 50% yield of furan [6].

An interesting procedure is that of BÖLCS [7], who treated furfurol with hydrogen in the presence of steam at 260—280°. Simple pumice-stone was applied as catalyst. ALIEV and coworkers [8] used metal alloys for the decarbonylation of furfurol. Metal alloys exhibit a number of advantageous properties. In the first place these are easily accessible, recoverable, and they are handled more easily than metal oxide catalysts. Good results have been achieved with a catalyst containing 65.6% aluminium, 23.9% zincum, and 10.4% iron. In ALIEV's opinion [9] these processes are actually decarbonylation, to the effect that the metal catalyst forms complex with the carbonyl group and the decomposition of this complex at higher temperature results metal carbonyl and furan. The reaction of the metal carbonyl with water results in the formation of the metal and formic acid, the latter decomposing to CO_2 and H_2. The supposed mechanism of the reaction is as follows (Equation 3):



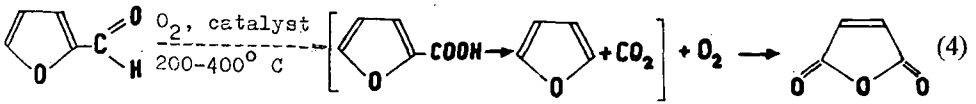
$$Me_n(CO)_z + X\,H_2O \rightarrow Me_n + X\,HCOOH$$
$$X\,HCOOH \rightarrow X\,CO_2 + X\,H_2 \qquad (3)$$

The mechanism of the decarbonylation reaction was also studied by VÁNDOR [10] in details. He stated that the decarbonylation reaction of furfurol gave only 30—40% yields of furan in the absence of steam, and the product contained mainly carbon monoxide. Since the low yield may be explained mainly by strong resinification, it seems obvious that in this case a direct decarbonylation takes place and the polymerization accompanied by resinification starts with the elimination of carbon monoxide. On the other hand, in the presence of steam 80—85% yields of furan are obtained and the end-product contains CO_2 and H_2 in equimolar amounts. The kinetic measurements of VÁNDOR have proved that the decarbonylation reaction of furfurol proceeds in the presence of excess steam approximately as a kinetically second order transformation. From this fact the conclusion may be drawn that the reaction is a Cannizzaro-type process, taking place in the vapour phase. The direct oxidation of furfurol to furoic acid followed by decarboxylation of the latter is not in accordance with the observed second order reaction, since furoic acid decarboxylates fairly fast and the partial pressure of water vapour is constant, as it may be expected at the Cannizzaro reaction. The authors wish to mention that the yields given in the literature could not be reproduced.

2. *Oxidative catalytic decarboxylation of furfurol*

The preparation of furan on a laboratory scale is carried out generally in the liquid phase through furoic acid. The procedure is based on the fact that furfurol transforms to 2-furoic acid in 90—95% yield in the presence of a catalyst consisting of NaOH, CuO, and some Ag_2O. 2-Furoic acid decarboxylates in quinoline in the presence of CuO catalyst in 70% yield [11]. The transformation of furfurol to 2-furoic acid proceeds also in the presence of other oxidizing agents. Thus, for instance, with H_2O_2 the reaction affords good yields [12]. There are also a number of procedures known for the decarboxylation process, to be carried out on a laboratory scale [13].

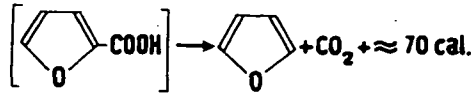
Contrary to the procedures known hitherto, the authors accomplished the production of furan from furfurol in the vapour phase under oxidative conditions [14]. The idea was taken from the investigations of MILAS and WALSH [15], who oxidized furfurol with the oxygen of air (with extremely high excess of oxygen) over V_2O_5 catalyst, to obtain maleic anhydride in good yields (Equation 4):



(4)

On basis of this result we concluded that as far as the process proceeds through furan, according to the mechanism described by the above authors [15], the selection of a suitable catalyst and reaction conditions would permit the elimination of further oxidation of furan. Accordingly furfurol was subjected to oxidative decaboxylation with air or oxygen; the reaction could be achieved without any significarnt over-

oxidation. The reaction carried out and studied in details by us is illustrated by Equation 5:



(5)

Comparison of the reaction heats of the processes represented by Equations 2 and 3 reveals that the reaction heat of the oxidative decarboxylation process carried out by us significantly higher than that of the preceeding reaction. Because of the high reaction heat a number of reactors of novel type have been developed by us for the effectuation of these reactions [16].

Experimental

I. Catalytic laboratory for the accomplishment of oxidative decarboxylation of furfural

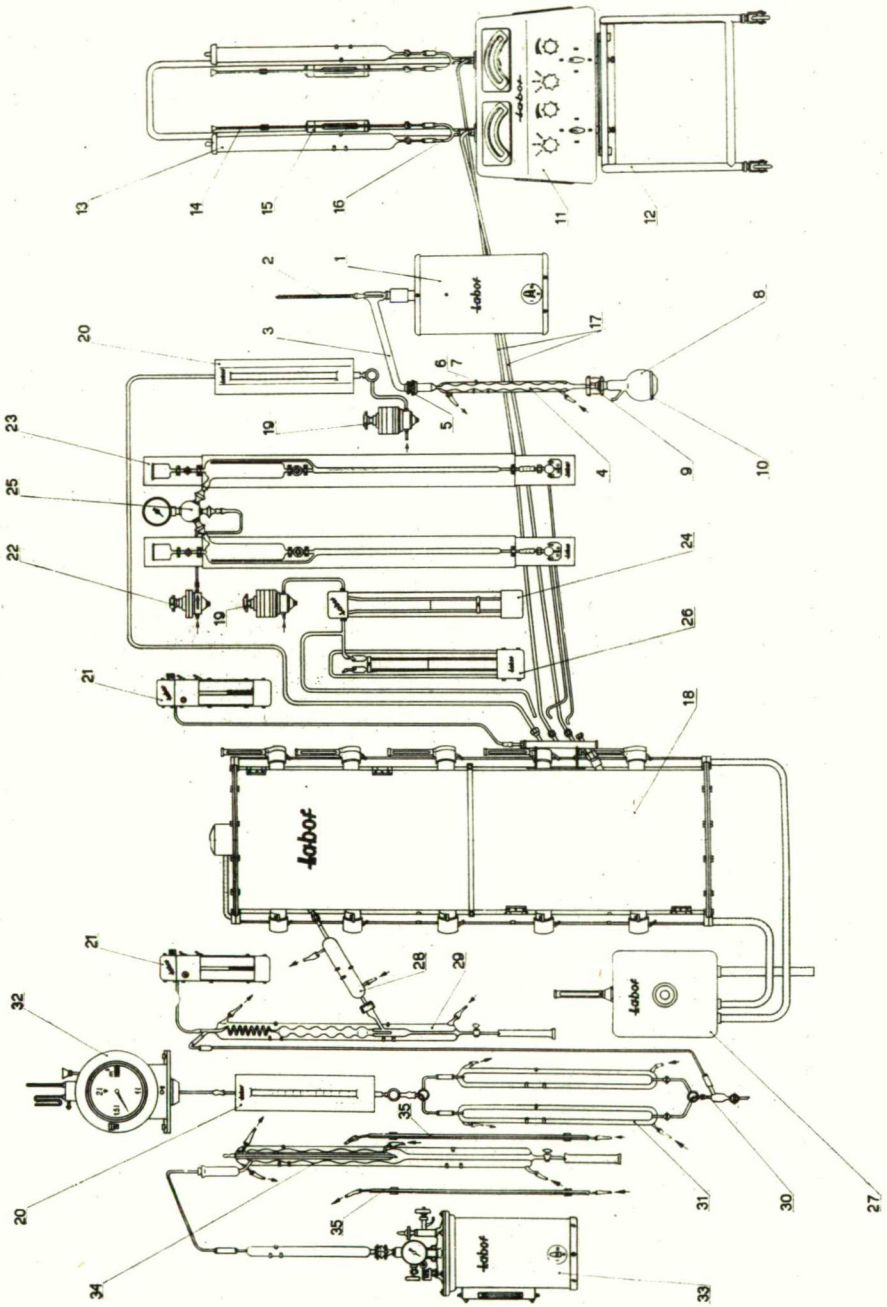
The experiences of a number of apparatus have helped us in developing the present form of our vapour phase, heterogeneous catalytic laboratory.

Iron, glass and quartz reactors have been employed for carrying out the reaction. Iron reactors have the disadvantage that the catalytic effect of the reactor-wall can not be avoided. To eliminate wall-effects glass and quartz reactors were used. The drawback of such reactors lies in the low heat conductivity of the wall, moreover the inaccurate fitting of the heating block caused strong local over-heatings, resulting in resinification of the starting material.

In catalytic oxidation reactions, among the structural materials coming into consideration nickel has the least pronounced undesired catalytic effect, therefore the reactor (18) of our apparatus to be described later (Fig. 1) was made of nickel. The temperature and heating of the reactor was controlled according to the five temperature-zones of the reactor by devices and switches placed on an electric instrumentboard. On this electric instrument-board the electric heat-characteristics of the reactor-sectors could be read off. The temperature of the heating sectors of the reactor were controlled by means of phototransistoric temperature-regulators and thus the temperature of the reactor-wall was kept at the desired value. This value was measured with bent, L-shaped, nitrogen-pressure mercury thermometers and recorded in six different colours.

Fig. 1. Flow sheet of the catalytic laboratory

1. Steel distillation flask, *2.* Ground glass distillation headpiece, *3.* Thermometer, 20—200 °C, *4.* Bulb condenser, *5.* Spherical ground joint clamp, *6.* Three-finger flask-holder, *7.* Double clamp-nut, *8.* Receiver, *9.* Ground joint holder, *10.* Holding ring, *11.* Feeding pump, *12.* Pipe trundle stand, *13.* Separating funnels, *14.* Burettes, *15.* Illuminator, *16.* Y-shaped glass connection tubes, *17.* Capillary pipe systems, *18.* Reactor, *19.* Pneumatic stabilized reductor, *20.* Rotameter, *21.* Phototransistoric pressure gauge, *22.* Pneumatic reductor, *23.* Fine feeder, *24.* Differential manometer, *25.* Glass T-tube, *26.* U-tube manometer, *27.* Thermostat for thermoelements, *28.* Metal Liebig-condenser, *29.* Coil and bulb condenser, *30.* Distributing cock-system with water jackets, *31.* Carbon columns, *32.* Gas meter, *33.* Evaporator, *34.* Combined cooler, *35.* Cooling walls.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The temperature in the axis of the reactor tube was measured with a three-fitting thermocouple and a connected millivoltmeter scaled in °C.

The freshly distilled furfural is introduced through the fine-dosing burette (23), the air through the stabilizing gauge (19) and differential manometer (24) into Sector I of the reactor. From the evaporator the reaction mixture enters catalyst-spaces II, III and IV. The reaction takes place here upon the contact surface and the vapours pass pre-cooler zone V and Liebig-cooler (28). The unreacted material condenses in the cooler and its amount can be read off in the lower part of the combined cooler-burette (29), wherefrom it can be let out through the tap to distill again for the next experiment. The uncondensed vapours and gases pass the bulb and coil condensers and reach the distributor head (30), from where in case of suitable tap-position they come to the carbon column (31). Furan is adsorbed here, while all the rest of the mixture goes further through rotameter (20) and gas-meter (32) to the exhausting equipment.

Desorption of furan is made with steam after saturation. The desorbed furan is collected in the furan-burette (34), where its volume, too, may be measured.

When larger amounts of fluid reaction-components are introduced, a motoric pump (11) is employed.

Experiments for the conversion of furfurol to furan

The oxidation of furfurol was carried out in the presence of the following catalysts: V_2O_5 on Al_2O_3, PbO on Al_2O_3, and PbO on aluminium grease, respectively. The temperature dependance of the reactions taking place on the above catalysts has been studied and expressed in yields and utilizations.

The definitions of the measure of value factors employed in our experiments are the following:

$$Te = \frac{\text{rate of feed of furfurol in ml/sec}}{\text{catalyst volume in liters}}$$

$$I = \frac{1}{\text{Te}}$$

$$A\% = \frac{\text{moles of furfurol converted}}{\text{moles of furfurol introduced}} \cdot 100$$

$$T\% = \frac{\text{moles of furan formed}}{\text{moles of furfurol introduced}} \cdot 100$$

$$K\% = \frac{\text{moles of furan formed}}{\text{moles of furfurol converted}} \cdot 100$$

a) Catalyst : V_2O_5 on Al_2O_3 (oxidation catalyst of the Hungarian Chemical Works)

Molar ratio of oxygen and furfurol:	2:1
Catalyst volume:	278 ml (V_2O_5)
Te (space velocity):	0,075 sec^{-1}
I (contact time):	13,0 sec
Temperature:	$a_1 = 250°$
	$a_2 = 300°$
	$a_3 = 350°$
	$a_4 = 400°$

	Temperature °C	A_{av}. %	T_{av} %	K_{av} %
a_1	250	22,6	—	—
a_2	300	30,8	0,55	1,8
a_3	350	54,8	15,2	27,4
a_4	400	68,1	2,4	3,5

b) Catalyst: PbO on Al_2O_3
Molar ratio of oxygen and furfurol: 2:1
Catalyst volume: 350 ml
Te (space velocity): 0,072 sec^{-1}
I (contact time): 13,8 sec
Temperature: $b_1=225°$
$b_2=250°$
$b_3=280°$
$b_4=300°$

	Temperature °C	A_{av} %	T_{av} %	K_{av} %
b_1	225	52,2	14,3	27,4
b_2	250	57,7	21,0	35,5
b_3	280	71,7	18,3	26,7
b_4	300	84,4	18,1	21,7

c) Catalyst: PbO on aluminium grease
Molar ratio of oxygen and furfurol: 1:0,8
Catalyst volume: 447 ml
Te (space velocity): 0,057 sec^{-1}
I (contact time): 17,6 sec
Temperature: $c_1=225°$
$c_2=250°$
$c_3=275°$
$c_4=285°$

	Temperature °C	A_{av} %	T_{av} %	K_{av} %
c_1	225	89,9	17,9	20,1
c_2	250	87,3	19,0	21,8
c_3	275	94,3	29,0	30,6
c_4	285	87,7	11,2	14,5

Preparation of the catalysts applied

a) V_2O_5 on Al_2O_3 supporter: the oxidation catalyst of the Hungarian Chemical Works

b) PbO on Al_2O_3 supporter: metal Al is dissolved in 50% NaOH solution and filtered to remove solid contaminations. A slow flow of CO_2 is passed through the solution at 80—90 °C, when crystalline $Al(OH)_3$ precipitates, which is then washed by decantation. The decanted product is mixed with 50(v)% minium to a homogeneous dough and partially dried. The obtained clay-like mass is passed through a hole of 3 mm. diameter and kept at room temperature until air-dry. The long rods are broken to pieces of 3—5 mm. length, dried with infra-lamp for

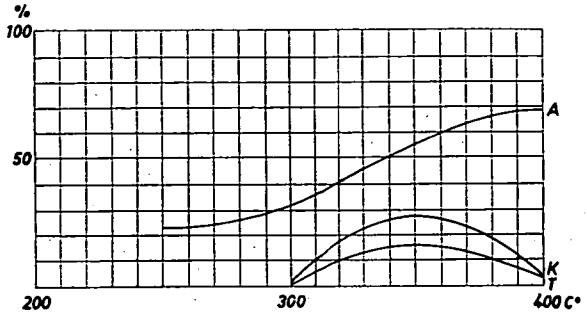

Fig. 2. Conversion of furfurol to furan. Temperature dependence of the measure of value factors. (V_2O_5 catalyst)

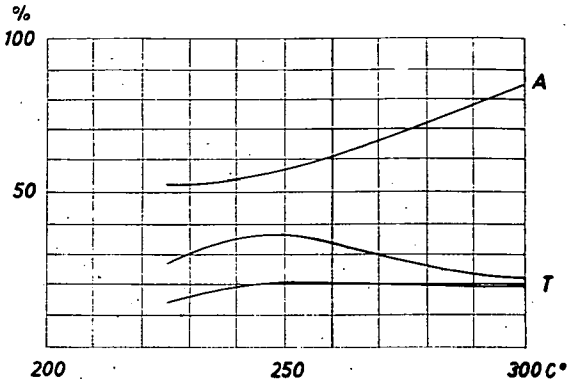

Fig. 3. Conversion of furfurol to furan. Temperature dependence of the measure of value factors. (PbO on Al_2O_3 catalyst)

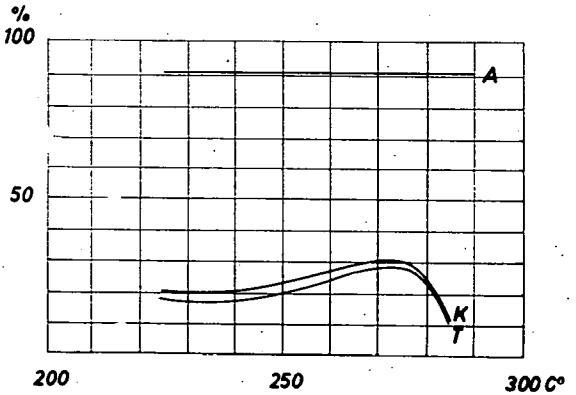

Fig. 4. Conversion of furfurol to furan. Temperature dependence of the measure of value factors. (PbO on aluminium grease catalyst)

5—6 hours, gradually heated at 350—450°, and kept at this temperature for 6 hours, the heating being repeated at 350—450° for a further 6 hours.

c) PbO on aluminium grease supporter: $Al(OH)_3$ is prepared as described above. The decanted product is mixed with 80(w)parts minium, the mixture is diluted with 20 parts water and shaken in a bolter for 30 minutes. Then aluminium grease is added, as to the suspension floods it and the whole is vigorously shaken for 1 hour again. After decantation the covered aluminium grease is dried with infra-lamp to air-dry and then gradually heated to 500—600 °C.

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ПРИМЕНЕНИЕ ФУРФУРОЛА. V

Способ и аппаратура для получения фурана из фурфурола с парофазным гетерогенным каталитическим методом

Л. Месарош, Г. Шобэл

Разработана каталитическая лаборатория для получения фурана, методом окисьлительного декарбоксилирования фурфурола. В отличие от до сих пор известных методов реакция проводилась в окислительных условиях на катализаторах V_2O_5/Al_2O_3, PbO/Al_2O_3, PbO/Al. Установлены оптимальные экспериментальные параметры реакции.